

**REACTION ANALYSIS OF THE FORMATION OF $CuInSe_2$ FILMS IN A
PHYSICAL VAPOR DEPOSITION REACTOR**

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The reaction kinetics for the formation of $CuInSe_2$ films by reacting Cu/In layers with elemental selenium are compared with those for H_2Se . The species mole fractions as a function of time in a single Se source PVD reactor are found to be essentially the same as those obtained in a CVD reactor with flowing H_2Se indicating that the same chemical equation representation can be used in both cases. The chemical engineering reaction analysis model previously developed ⁸ is shown to adequately predict experimental data in both reactors. The model is employed to predict three source behavior. The effect of rate of species delivery and substrate temperature on the time to make $CuInSe_2$ is quantitatively presented.

INTRODUCTION

Considerable success in making high efficiency $CuInSe_2$ and related alloys with *Ga* and *S* devices has been achieved in a variety of laboratory scale batch reactors. These reactors differ in the delivery of the reacting species, the starting precursor and the temperature time profile in the growing film. These reactor systems are summarized below:

- Physical Vapor Deposition (PVD) Reactors:

Direct line of sight delivery of the reacting species to the substrate in three or four source (gallium) reactors has been extensively studied. The highest efficiency devices have been produced in such reactors.¹⁻³

Copper and Indium layers can also be selenized in a PVD reactor using a single selenium source.⁴

- Chemical Vapor Deposition (CVD) Reactors:

Successful devices of efficiencies between 12 and 14% have been achieved in CVD reactors using flowing H_2Se to selenize copper indium layers.^{5,6}

- Rapid Thermal Processing (RTP) Reactor:

In this method of producing copper indium diselenide, elemental copper, indium (gallium) and selenium are deposited at room temperature by various methods and the stack is then very rapidly heated to over 500°C and reacted.⁷

A reactor independent reaction analysis of $CuInSe_2$ growth would greatly aid in preliminary commercial scale reactor design and costing so business decisions can be made regarding the best process for commercial scale production of modules. We have previously presented a chemical engineering reaction analysis of $CuInSe_2$ growth using concentration time data taken at various temperatures (250°C, 325°C, and 400°C) in a CVD reactor with flowing H_2Se .^{8,9} The experimental analysis was carried out in the tubular CVD reactor because we were able to remove samples from the reaction zone, and

obtain time progressive species concentration data. Using this data a mathematical model for $CuInSe_2$ growth was developed. The purpose of this paper is to compare concentration time data obtained in a PVD reactor using a single selenium source to selenize copper indium layers with the data and the model predictions from the CVD reactor. The experiments were carried out in a laboratory scale PVD reactor which was modified to obtain time progressive data by installing a film cooling assembly inside the bell jar.¹⁰

EXPERIMENTAL

The precursor metal films were deposited on a molybdenum coated sodalime glass. A magnetron sputtering system was used to deposit 2500 Å of copper followed by 6150 Å of indium to give an atomic ratio of 0.9 and a final $CuInSe_2$ thickness of about 2 µm. The *Cu-In* bilayers were annealed in an inert atmosphere for 20-30 minutes prior to selenization.

The tubular CVD reactor used and the methodology followed was described earlier.⁸ The PVD reactor consists of a bell jar and is equipped with a Varian model 183 diffusion pump. The operating pressure was 8×10^{-6} torr. Elemental selenium is evaporated from a Knudsen-type source bottle made of Corning Macor.¹⁰ A cooling assembly is installed inside the reactor where the substrate can be moved into an enclosure and rapidly cooled with direct contact helium flow.

The annealed Cu/In bilayers are placed on the substrate heater and heated to 400°C at a rate of 15.5°C per minute. The bottle heatup was initiated when the substrate heater reached 180°C. The substrate temperature and selenium deposition rates stabilized after approximately 35 minutes, at which time the shutter was opened. The power to the

Se was adjusted during the reaction to maintain a selenium deposition rate of approximately 10 Å per second. At the end of the desired time interval, the substrate heater is turned off and the substrate is moved to the cooling assembly by means of a swing arm. Helium flow is started and the substrate is cooled from 400°C to 150°C in about 15 seconds. The cooling system is described in detail elsewhere.¹⁰ The selenization reactions were carried out isothermally at 400 °C and samples were reacted for time periods ranging from 30 seconds to 30 minutes.

The samples were then analyzed using x-ray diffraction to identify phases and estimate the relative mole fraction of the identified phases. Theoretically, the peak intensity is directly proportional to the volume fraction of the species for a homogeneous sample showing no preferential orientation. This relation is applied using single phase thin film standards to determine the volume fraction of individual species in the reacted samples. Thin films of *Cu*, *In*, *Cu/In* alloy, *In₂Se* and *CuInSe₂* were analyzed by XRD to establish quantitative standards. The texture of the standard films was compared with that of reacted films to ensure the validity of the analysis. For all films analyzed there were no detectable differences between the orientation of standards and reacted films. The method of analysis has been described in detail elsewhere.⁸

RESULTS

The species identified during film growth in the PVD reactor are shown in Table 1. These are the same species previously identified during film growth in the CVD reactor. The mole fraction of each identified species as a function of time is calculated from the XRD data and presented as crosses in Figure 1. Also plotted in the same figure as solid circles are the mole fractions of species obtained in the CVD reactor.⁸ The plots show that the species concentrations as a function of time are about the same for both reactors.

This suggests that the same selenium species are present in both reactors and that in the CVD reactor the hydrogen selenide decomposes on the growing film surface to selenium.

The model developed in the CVD reactor takes into account the presence of a variety of Cu/In species, represented as Cu_xIn_y coexisting at the reaction temperatures. The model equations are solved with a x:y ratio ranging from 1 to 2 representing two limiting cases, the reaction of $CuIn$ and Cu_2In . The intermediate cases will fall in between. The model predictions for these two limiting cases are shown by the dashed ($CuIn$) and the solid lines (Cu_2In) in Figure 1. Inspection of Figure 1 shows that data obtained in both reactors are in reasonable agreement with each other and well within the experimental accuracy of the XRD measurement. The agreement between data and prediction indicates that the overall chemical equation description and our assumed kinetic rate expressions are adequate to characterize film growth in both reactors. Since the rate expressions contain a selenium concentration term which we have assumed to be constant it appears that this assumption is valid and that there is probably excess selenium in both the CVD and PVD reactors.

MODEL BEHAVIOR AND PREDICTIONS

The ability of the chemical engineering reaction model to estimate concentration-time profiles in the single source PVD selenization reactor suggests that the model can be used to predict behavior in the three source PVD reactor. For the three source reactor, it is assumed that there is no Cu/In alloy, (Cu_xIn_y), and thus, the chemical equations previously presented must be altered to allow for reaction with copper. The model equations must also be modified to include rate of incorporation of elemental Cu and In in the film. Table 2a presents the original chemical equations obtained from the CVD experiments and the specific reaction rate constants. These chemical equations were proposed based on the identified species and the comparison of the model behavior with

species concentration-time data. A large number of chemical equations were examined, many of which were found to be incapable of predicting experimental concentration-time data. The set which described the observed data best is presented in Table 2a. The detailed procedure is explained in our earlier publication.⁸

For the three source reactor, it is assumed that the reaction follows a similar path and that copper, indium and selenium do not react directly to form $CuInSe_2$. Table 2b shows the proposed chemical equations for the three source PVD reactor. Table 3 shows the reaction model equations based on Table 2b and modified to include $r_i(In)$ in the indium component balance and $r_i(Cu)$ in the copper component balance. These terms account for the rate of incorporation of indium and copper in the growing film. The rate of incorporation denotes the amount of species that contributes to the film growth, *i.e.*, it is the amount that is delivered to the surface less the amount that re-evaporated. As in the case of CVD analysis, the model equations are solved assuming constant selenium concentration.

The behavior of the CVD and PVD models are shown in Figure 2, a plot of $CuInSe_2$ concentration in the film as a function of time at 400° C. The model prediction curves use the specific reaction rate constants in Table 2. The solid line is the model prediction for the CVD explained in detail elsewhere^{8,9} and is included in Figure 2 for comparison purposes. The model equations used for obtaining the CVD reactions differ from those presented for the three source PVD reactor (Table 3) in that there is no rate of delivery term in the indium balance and a species balance on Cu_xIn_y (x=2, y=1, Table 2) is used instead of the copper balance. The solid circles are experimental data obtained in the CVD reactor.

The dashed line designated “A” is the model prediction for the IEC three source PVD batch reactor producing a 2 μ m $CuInSe_2$ film.³ Typical source and substrate

temperatures versus time for the IEC reactor are shown in Figure 3.³ The model equations in Table 3 are solved using a copper incorporation rate, $r_i(Cu)$, of 7.4×10^{-7} moles/min for 30 minutes and an indium incorporation rate, $r_i(In)$, of 6.2×10^{-7} moles/min for 40 minutes. The dashed line designated as “B” shows the effect of increasing the rate of incorporation of both metals by a factor of five.

The dashed line designated as “C” is the limiting case when it is assumed that both metals are instantaneously delivered to the substrate at time equal to zero. To produce “C”, the model equations in Table 3 were solved with $r_i(In)$ and $r_i(Cu)$ set equal to zero. The required amount of indium and copper was put into the respective component balance equations as an initial condition. The slight discrepancy between the solid curve and curve “C” may indicate the difference between using the bimetallic alloy Cu_xIn_y in the formation of $CuInSe_2$ versus using the metals. The interesting result of the model predictions is that it takes approximately 15 minutes to form $CuInSe_2$ film at $400^\circ C$ even if the copper and indium are delivered at an infinite rate. Another conclusion of the model prediction in Figure 2 is the reduction in time to complete the reaction if incorporation rates are increased by a factor of five (curve “B”). These are important results with significant impact on commercial scale reactor design because one can predict holding time in the reactor as a function of species delivery rate, a quantity directly related to rate of incorporation, and thus can optimize the reactor design and its performance. Substrate temperature is also a critical variable affecting reactor design. Since we have obtained energies of activation⁸ (Table 3) the model can be used to predict performance at any temperature. The solid lines in Figure 4 show the model predictions for the three cases “A”, “B” and “C” for a substrate temperature of $500^\circ C$. Although energies of activation are not tabulated for Cu and In , extrapolation of experimental results obtained at $250^\circ C$, $325^\circ C$ and $400^\circ C$ show that selenization of In and Cu takes place instantaneously at $500^\circ C$. Also plotted in Figure 4 are the predictions at $400^\circ C$ for comparison. The

increase in substrate temperature greatly reduces the time to form a $CuInSe_2$ film for all three cases.

CONCLUSIONS

The species compositions as a function of time are essentially the same for $CuInSe_2$ films formed from the reaction of $Cu-In$ layers using hydrogen selenide in a CVD reactor or elemental selenium in a PVD reactor. The chemical equation representation used to model the growth of $CuInSe_2$ film is shown to adequately predict experimental concentration time profiles in both these reactors. This indicates that the rate of selenium incorporation into the film is the same for both H_2Se and elemental selenium. It also suggests that the reaction analysis is reactor independent and that it can be applied to any reactor making $CuInSe_2$. The kinetic model for the formation of $CuInSe_2$ allows a means to quantitatively design a commercial scale reactor. The three source model predictions show that rate of incorporation of metals into the growing film is a critical parameter for determining reactor holding time in this type of reactor.

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FIGURE CAPTIONS

Figure 1. Mole fraction of species versus time. Comparison between the CVD and single source PVD reactor. (h) experimental data obtained in CVD reactor with H_2Se , (x) experimental data obtained in single Se source PVD reactor. (-----) model predictions with $CuIn$, (___) model predictions with Cu_2In .
(a) $CuIn$, (b) Cu_2In , (c) In_2Se , (d) $InSe$, (e) $CuInSe_2$.

Figure 2. Model predictions for three source PVD reactor at $400^\circ C$. (.....) “A”: for IEC procedure.³ (---) “B”: for delivery rates five times those in curve A. (....) “C” for instantaneous delivery of species. (i) experimental data obtained in CVD. (___) model prediction for CVD.

Figure 3. Source and substrate temperature versus time profile for the IEC three source PVD reactor.³

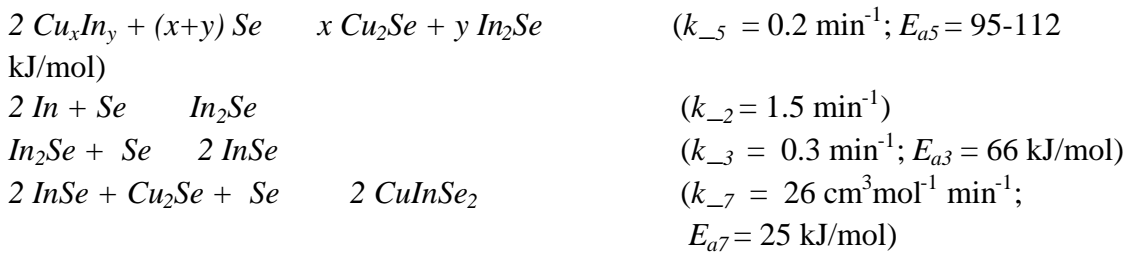
Figure 4. Effect of temperature on model predictions for the three source PVD reactor. Solid lines for cases “A”, “B” and “C” for a substrate temperature of $500^\circ C$. (.....) A, (---) B and (....) C for a substrate temperature of $400^\circ C$.

Table 1. Copper-indium Bilayer Selenization in the Single Source PVD Reactor at 400 °C - Summary of XRD Results

Time (min.)	Phases Observed		
	<i>metals</i>	<i>binary selenides</i>	<i>ternary selenides</i>
0.5	Cu_xIn_y, In	In_2Se	
1	Cu_xIn_y, In	$In_2Se, InSe$	
2	Cu_xIn_y	$In_2Se, InSe$	$CuInSe_2$
5	Cu_xIn_y	$In_2Se, InSe$	$CuInSe_2$
10	Cu_xIn_y	$In_2Se, InSe$	$CuInSe_2$
20		$InSe$	$CuInSe_2$
30		$InSe$	$CuInSe_2$

Table 2. Reaction Pathway, Rate Constants at 400° C and Activation Energies ^{8,9}

a) CVD analysis selenization of copper indium bilayers:



b) Proposed PVD three source analysis for selenization of elemental copper and indium:

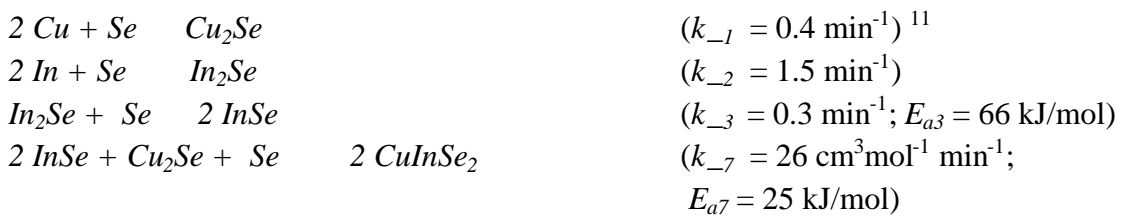


Table 3. Reaction Analysis Model Equations Modified for Multisource PVD Reactor

$$\frac{d([In] V_f)}{dt} = -2k_2 [Se] [In] V_f + r_i (In) = -2k_2' [In] V_f + r_i (In)$$

$$\frac{d([In_2Se] V_f)}{dt} = (k_2 [Se] [In] - k_3 [Se] [In_2Se]) V_f = (k_2' [In] - k_3' [In_2Se]) V_f$$

$$\frac{d([InSe] V_f)}{dt} = (2k_3 [Se] [In_2Se] - 2k_7 [Se] [InSe] [Cu_2Se]) V_f = (2k_3' [In_2Se] - 2k_7' [InSe] [Cu_2Se]) V_f$$

$$\frac{d([Cu] V_f)}{dt} = -2k_1 [Se] [Cu] V_f + r_i (Cu) = -2k_1' [Cu] V_f + r_i (Cu)$$

$$\frac{d([CuInSe_2] V_f)}{dt} = (2k_7 [Se] [InSe] [Cu_2Se]) V_f = (2k_7' [InSe] [Cu_2Se]) V_f$$

$$\frac{d([Cu_2Se] V_f)}{dt} = (k_1 [Se] [Cu] - k_7 [Se] [InSe] [Cu_2Se]) V_f = (k_1' [Cu] - k_7' [InSe] [Cu_2Se]) V_f$$